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Title: Summary of Summer Project: Evaluating New Double Perovskite Halide Scintillators for Radiation Detection Applications

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Summary of Summer Project:

Evaluating New Double Perovskite Halide Scintillators for Radiation Detection Applications

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Materials Science and Technology (MST) Division

MST-8 Materials Science in Radiation and Dynamics Extremes

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Project Outline

- Experimental validation of machine learning based prediction models
- Evaluating double perovskite halides (chlorides, some bromides)
  - $A_2BB'X_6$:Ce
  - A = Rb^+, Cs^+
  - B = Na^+, K^+
  - B' = RE^{3+}
  - X = Cl^-, Br^-
- Performing single crystal growth and characterization (physical, optical, scintillation properties)

Physics-informed machine learning for inorganic scintillator discovery

Cite as: J. Chem. Phys. **148**, 241729 (2018); https://doi.org/10.1063/1.5025819
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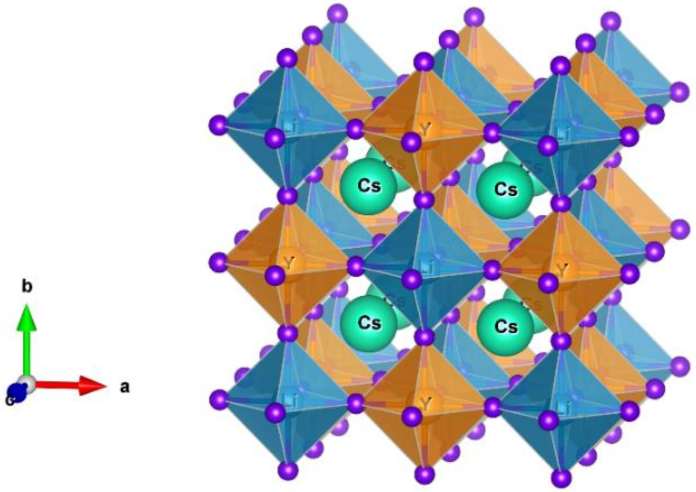
G. Pilania, K. J. McClellan, C. R. Stanek, and B. P. Uberuaga

Double perovskite structural model (Cs_2LiYCl_6)



Cubic space group *Fm*-3*m*

Selection Criteria

- For the typical scintillator, activator ground and excited states required to lie within the host bandgap
- Selected compounds w/ favorable positions of Ce^{3+} 5d and 4f states relative to conduction band (CB) and valence band (VB)

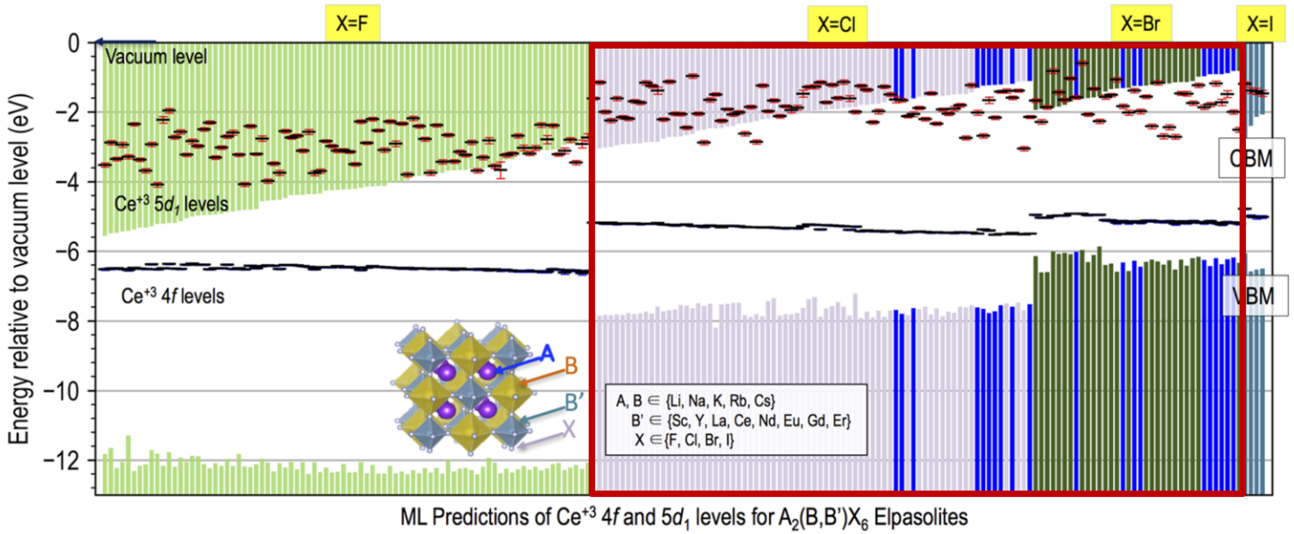


FIG. 8. A stacked band scheme showing the DFT-computed relative valence and conduction band edge alignments and the ML-predicted VRBEs of an electron in the Ce^{3+} activator's $4f$ and $5d_1$ levels for the elpasolite compounds. The compounds are grouped according to the halide chemistries and within each class the compounds are arranged according to the conduction band edge positions with respect to the vacuum level. Previously known scintillating compounds are highlighted with blue bars.

G. Pilania *et al.* "Physics-informed machine learning for inorganic scintillator discovery" J. Chem. Phys. **148**, 241729 (2018)

Objectives

1. Determine if scintillation occurs (do we get radioluminescence emission?)
2. Provide experimental data to feed back in to prediction models
3. Identify promising compositions to pursue further (which compounds have highest light yield)

Initial List of Compositions to Pursue Experimentally

Composition	Bandgap (eV)	Density (g/cm3)	Zeff	Melting Point (°C)
$Rb_2NaLaCl_6$:Ce	4.662	2.67	39.1	unknown
$Rb_2NaGdCl_6$:Ce	3.056	2.93 - 3.11	43.5	unknown
Rb_2NaYCl_6:Ce	5.124	2.61 - 2.77	30.7	unknown
Cs_2KGdCl_6:Ce	3.144	3.02 - 3.22	49.3	unknown
Cs_2KYCl_6:Ce	~5	2.92	42.7	unknown

*bandgap values obtained from materialsproject.org

- **Additional details**
  - Single crystals being grown via vertical Bridgman method
  - Melting points will need to be measured using DSC prior to growth
  - Using a Ce concentration of 2 mol%
    - 10% is optimal for ER and LY in some elpasolites, concern would be phase stability

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Plans for Partial Substitution of RE^{3+} w/ Bi^{3+}

- Purpose is to increase the Z_{eff}
- Other benefits
  - May reduce hygroscopicity
  - Smaller bandgap potentially leads to higher light yield
  - Same compounds with full Bi^{3+} replacement exist and have same cubic crystal structure (should form solid solution)
- Anticipated challenge:
  - Each compound is synthesized by melting above highest melting point (binary) constituent
  - Synthesis w/ Bi will be difficult due to low boiling point of $BiCl_3$ (T_m = 230 °C ; **T_b = 430 - 447 °C**)

$$Y = \frac{E_\gamma}{\beta \cdot E_g} S \cdot Q$$

Composition	Highest T_m component (°C)	Lowest T_m component (°C)	Synthesis Temp. (°C)
Rb2NaLaCl6:Ce	858	718	900
Rb2NaGdCl6:Ce	817	609	865
Rb2NaYCl6:Ce	817	718	865
Cs2KGdCl6:Ce	817	609	865
Cs2KYCl6:Ce	817	645	865

Estimated Increase in Z_{eff}

- Calculated Z_{eff} using →
- More robust methods for calculating Z_{eff} exist, however, this should give close approximation
- Initial candidates for Bi subst. will be (based on Ghanshyam's band structure calculations)
  1. $Rb_2NaLaCl_6$
  2. Rb_2KLaCl_6

$$Z_{eff} = \sqrt[m]{\sum f_i Z_i^m}$$

m = 2.94
f_i = the relative electron fraction of the ith element
Z_i = atomic number of ith element

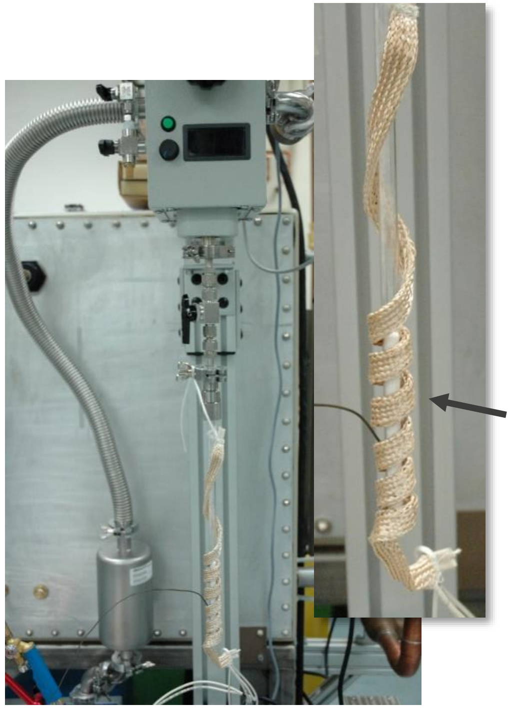
Composition	Bandgap (eV)	Density (g/cm3)	Zeff	Zeff (50% Bi3+ subst.)	RE3+ radius CN=6 (Angst.)	Bi3+ radius CN=6 (Angst.)	Ce3+ radius
Rb2NaLaCl6:Ce	4.662	2.67	39.1	50.3	1.032	1.03	1.01
Rb2NaGdCl6:Ce	3.056	2.93 - 3.11	43.5	51.6	0.938	1.03	1.01
Rb2NaYCl6:Ce	5.124	2.61 - 2.77	30.7	48.6	0.90	1.03	1.01
Cs2KGdCl6:Ce	3.144	3.02 - 3.22	49.3	54.9	0.938	1.03	1.01
Cs2KYCl6:Ce	~5	2.92	42.7	52.9	0.90	1.03	1.01
Rb2NaBiCl6	3.797	3.11	57.3				
Cs2KBiCl6	4.062	3.18 - 3.54	59.3				

*bandgap values obtained from materialsproject.org

Special Handling of Raw Materials Required Due to Hygroscopicity

- Halides tend to be hygroscopic (sensitive to moisture in air)
- Need to encapsulate material to prevent degradation
- Material is sealed in quartz ampoule prior to synthesis and growth

Raw material is dried under vacuum to remove moisture / hydrates

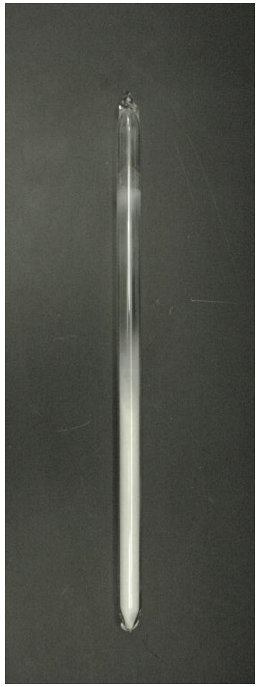


Heat tape around quartz ampoule

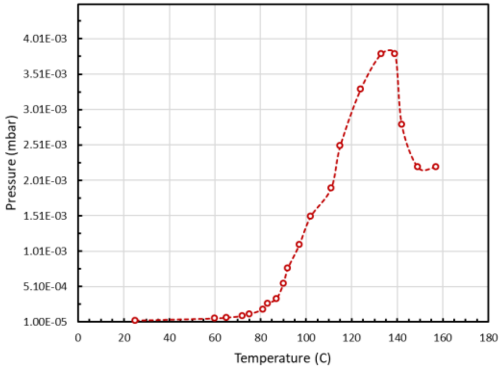
Pressure reaches 10^{-5} mbar before sealing

Seal with torch

Encapsulated and dried powder, ready for synthesis

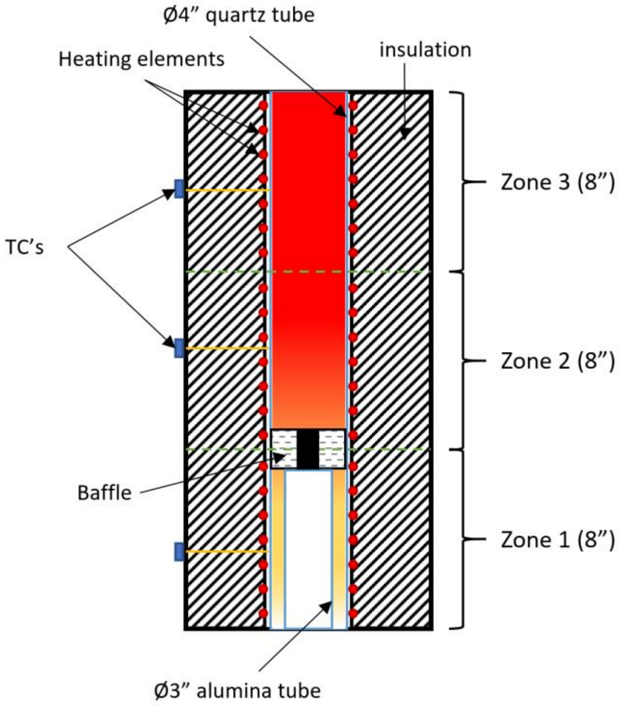


Pressure change during drying indicates removal of water



Synthesis and Crystal Growth Details

- **Prepared two sets of each sample**
  1. 3 gram charge, melt synthesis only → physical properties (DSC and XRD)
  2. 8 gram charge, for crystal growth → scintillation properties
- **Initially growing crystals 8 mm in diameter**
  – Small size allows for quicker screening
- **Growth parameters**
  – Bridgman growth in 3-zone furnace equipped w/ thermal baffle
  – Translation rate: 0.8 mm/hr
  – Cooling rate: 5-7 °C/hr

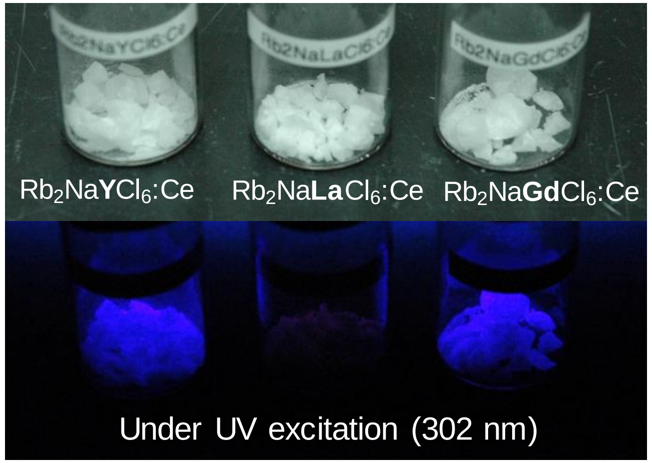


Results

Successfully Synthesized Rb_2NaYCl_6:Ce, and $Rb_2NaGdCl_6$:Ce

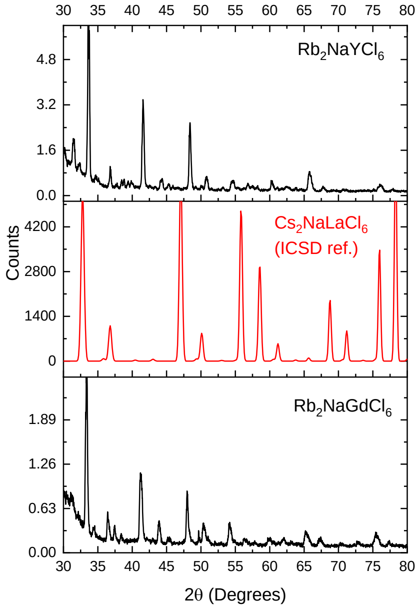
- Melt-synthesized material at 900 °C
- Measured XRD in air-tight holder
- Primary phase is cubic elpasolite (space group F*m*-3*m*)
- Low intensity peaks from unknown secondary phase(s) also observed
  - Expected due to incongruent melting

Synthesized polycrystalline samples

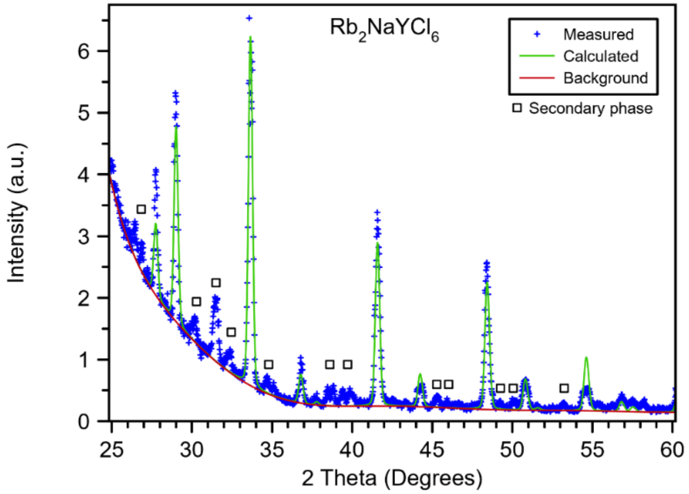


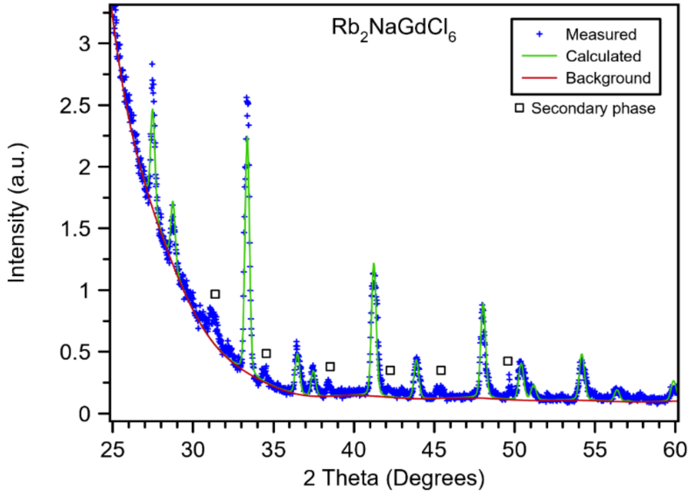
XRD Sample Holder

Measured XRD vs Reference



Rietveld Refinement

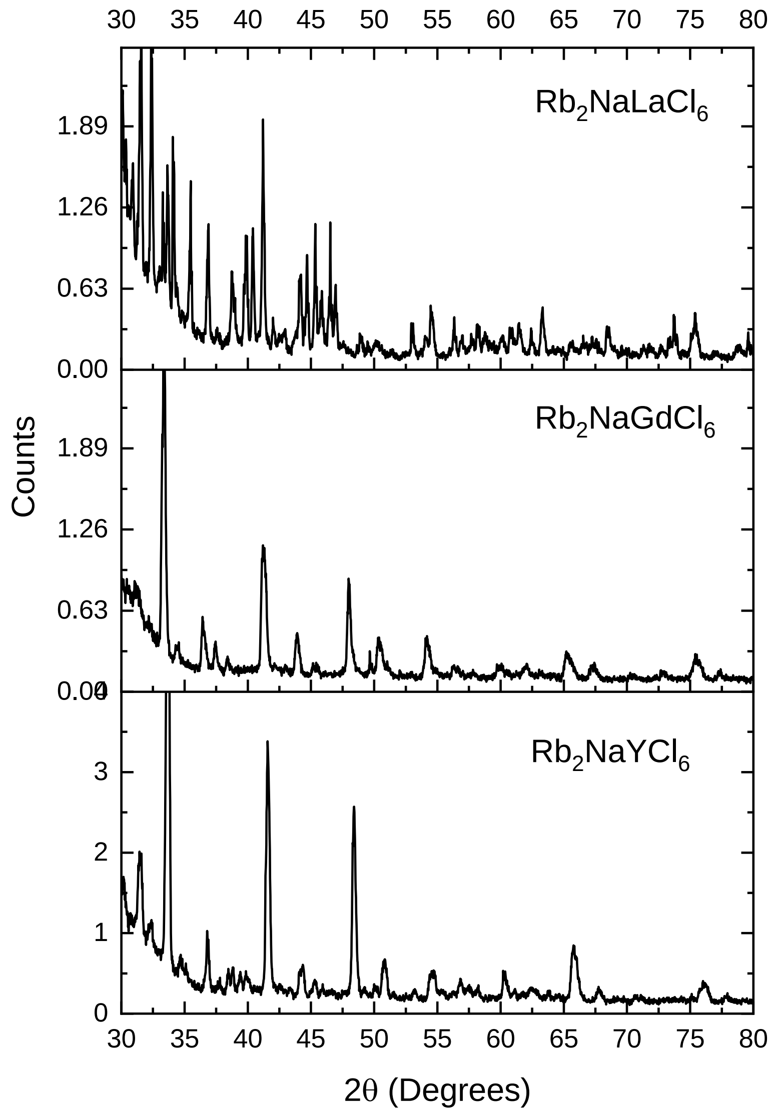




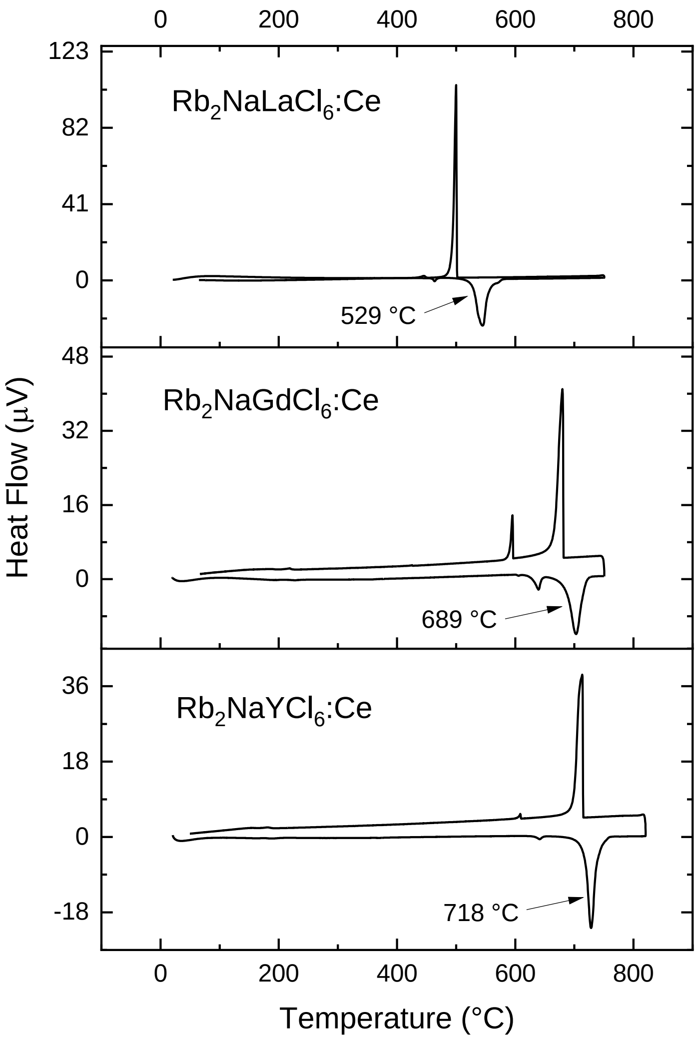
$Rb_2NaLaCl_6$:Ce Doesn't Appear to Form Cubic Structure

Still analyzing / in the process of identifying the phase(s)

X-ray Diffraction



DSC Measurements Reveal Incongruent Melting

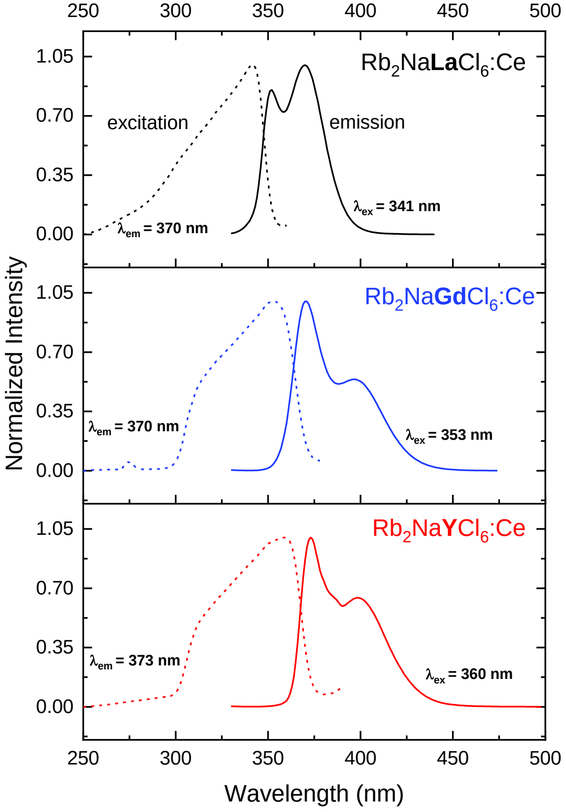


- Measured in sealed quartz crucibles
- 10 k/min heating and cooling rates
- Able to obtain melting points (needed for setting growth parameters)
- Multiple endothermic and exothermic features are present → incongruent
- Should still be able to produce a single-phase crystal

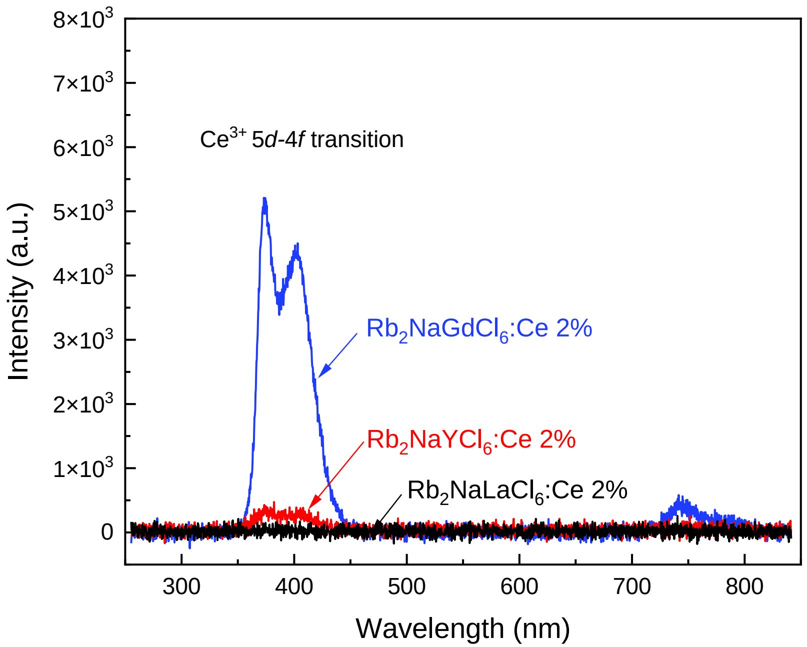
Luminescence and Scintillation is Observed, as Predicted

- Measured melt-synthesized samples
- All three compositions luminesce
- $Rb_2NaGdCl_6$:Ce is most promising, highest intensity RL emission
- RL emission not observed for La compound, weak emission from Y compound

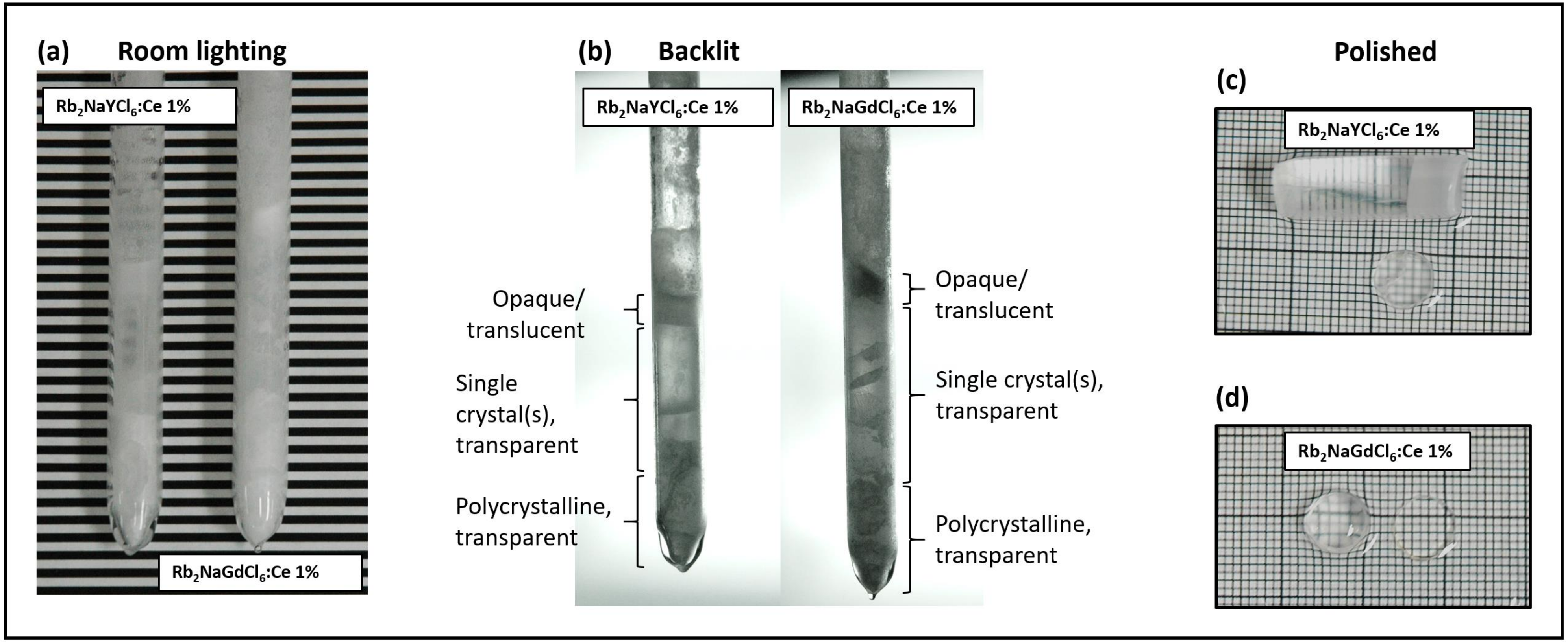
Photoluminescence



Radioluminescence

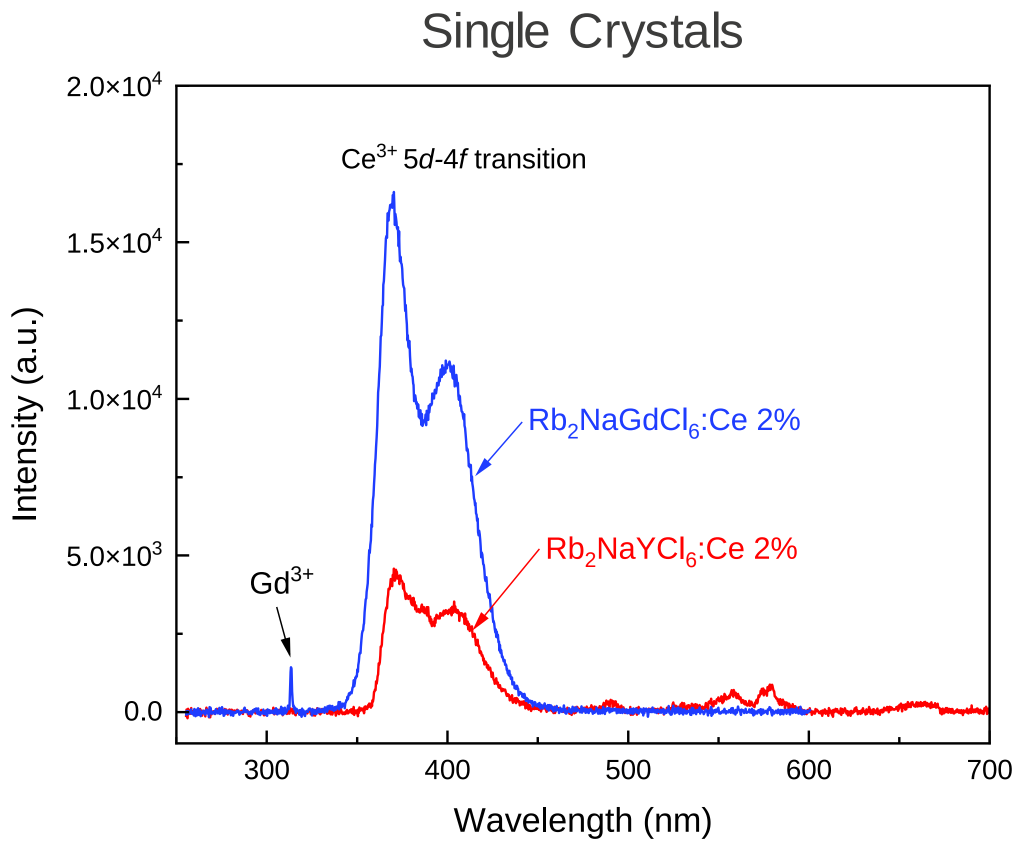


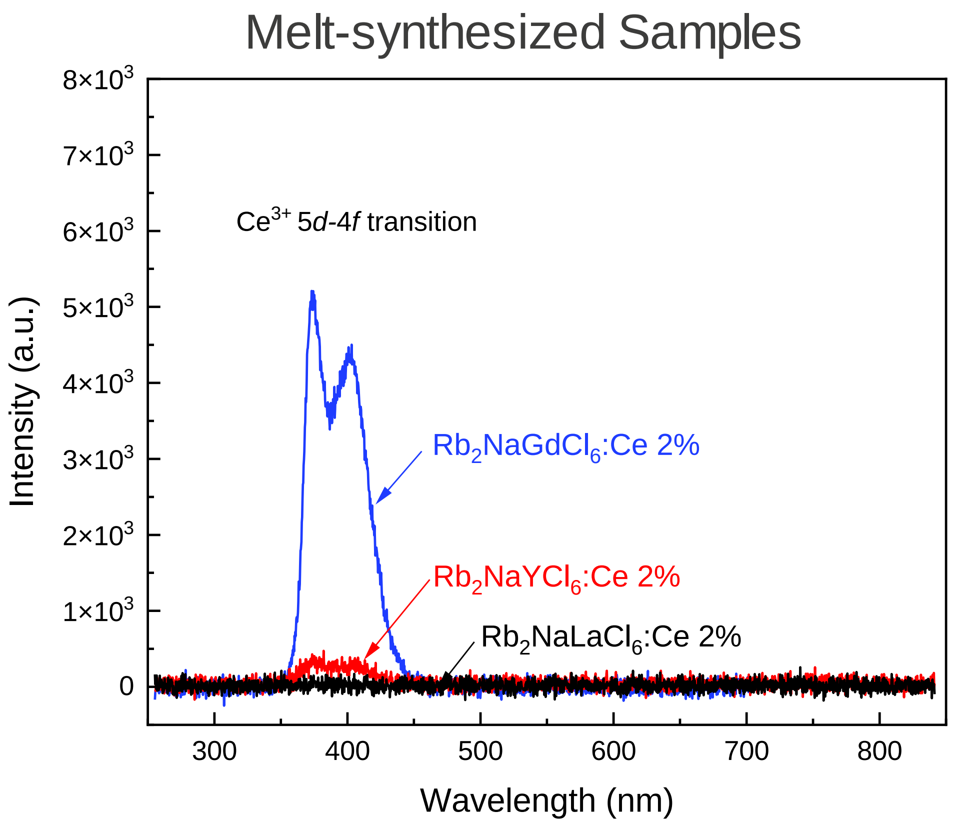
Successful 1st Attempt at Crystal Growth: Rb_2NaYCl_6:Ce and $Rb_2NaGdCl_6$:Ce



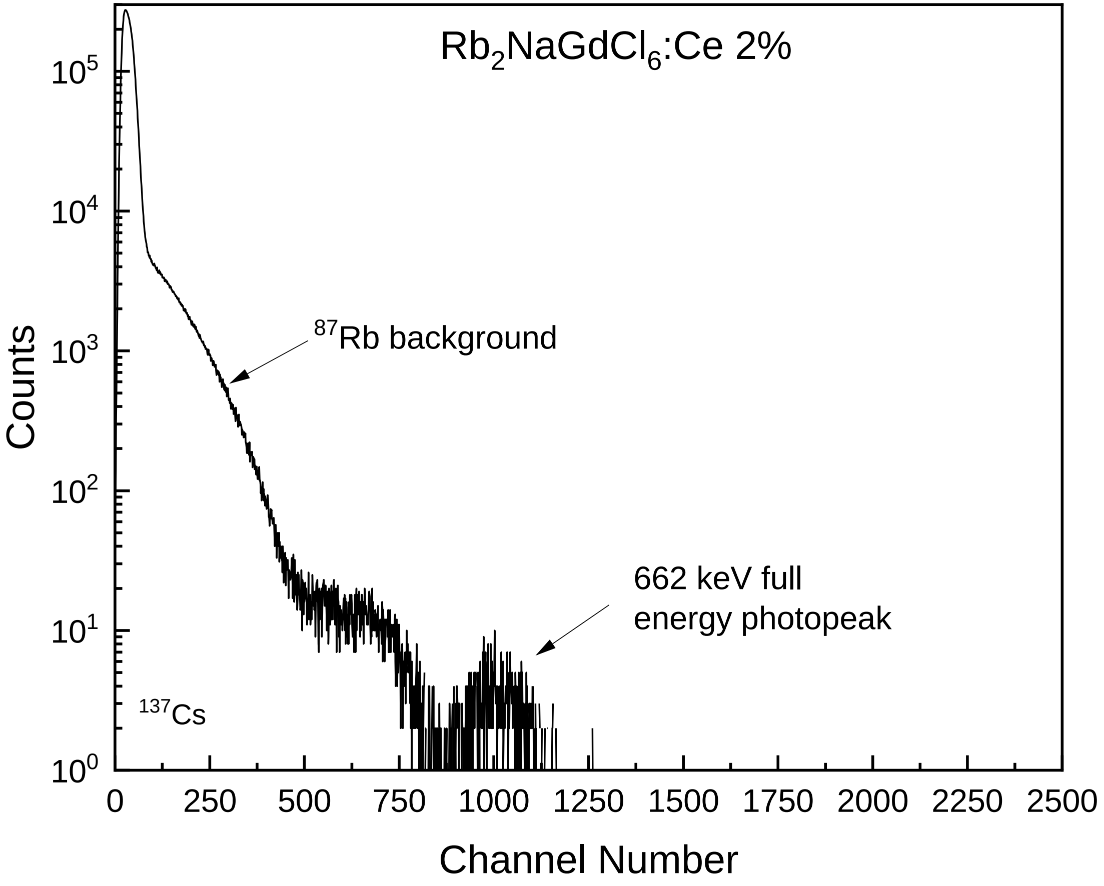
- Opaque section (at top) is a result of incongruent melting
- Transparent polycrystalline section may be due to poor seeding
- XRD necessary to assess compositional uniformity

Radioluminescence Observed for Single Crystals, Higher Intensity Than M-samples

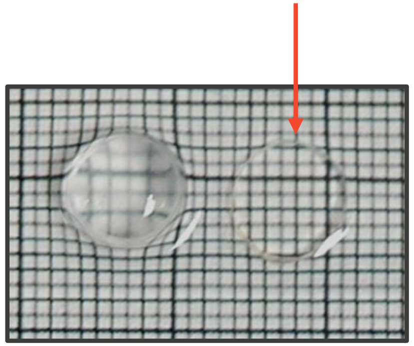




$Rb_2NaGdCl_6$:Ce Pulse Height Spectrum



Measured on Ø8 mm x ~2 mm thick slab



CAEN amplifier and digitizer used for pulse processing

$Rb_2NaBi_{0.5}La_{0.5}Cl_6$:Ce Synthesis

525 °C for 18 hours

550 °C for 45 minutes

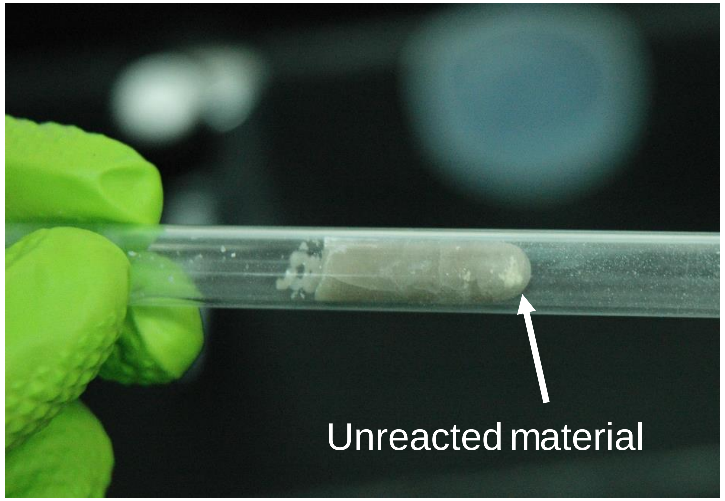
575 °C for 1 hour

- Attempted to synthesize at low temperature due to low boiling point of $BiCl_3$
- No gas / vapor (from boiling of $BiCl_3$) could be visibly detected
- Appear to be able to synthesize below T_m of all constituents

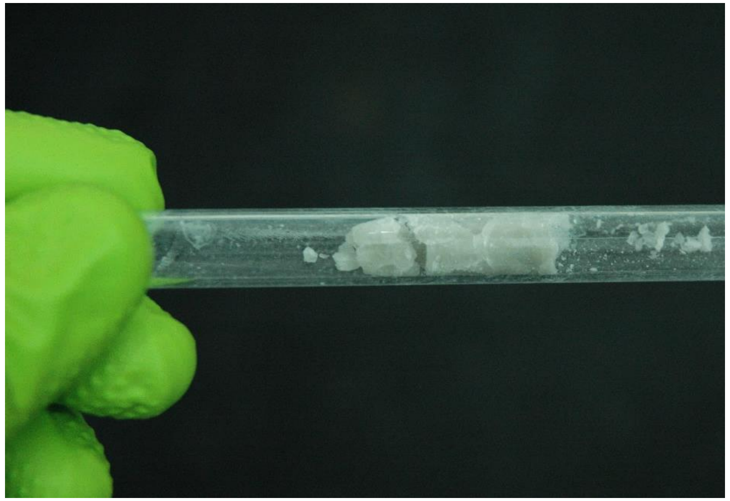
Component	Melting Point (°C)
RbCl	718
NaCl	801
$LaCl_3$	858
$CeCl_3$	817
$BiCl_3$	**230 (T_b = 430)**

Additional Synthesis of $Rb_2NaBi_{0.5}La_{0.5}Cl_6$:Ce at Higher Temperature to Ensure Full Mixing

After synthesis at 575 °C for 5 hours



After synthesis at 775 °C for 16 hours

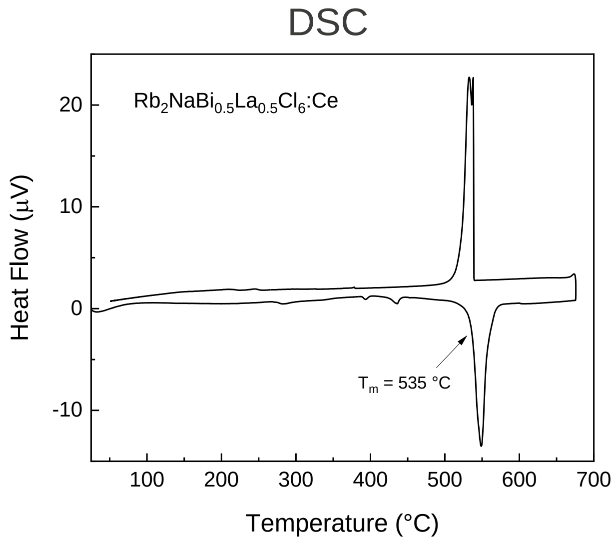


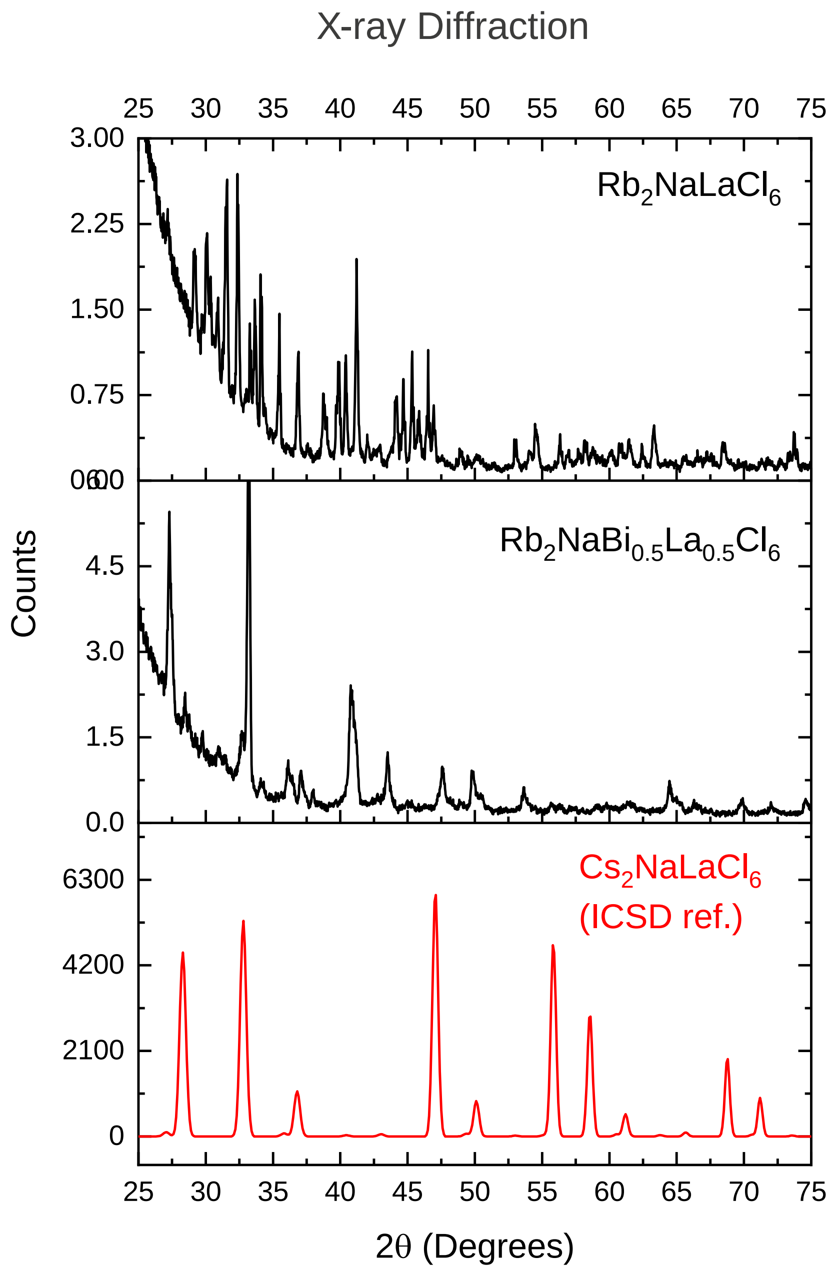
After synthesis at 830 °C and comparison with $Rb_2NaLaCl_6$:Ce

Solidified material has a gray-white appearance, as opposed to $Rb_2NaLaCl_6$:Ce which is white

Substitution w/ Bi^{3+} Appears to Stabilize the Cubic Elpasolite Phase

- $Rb_2NaLaCl_6$ did not crystallize in the cubic structure
- $Rb_2NaBi_{0.5}La_{0.5}Cl_6$ consists primarily of the cubic elpasolite phase
  - Contains some low intensity impurity-related peaks
  - Similar to $Rb_2NaGdCl_6$ and $Rb_2NaLaCl_6$ as a result of incongruent melting





Summary

- 3 new compounds were synthesized ($Rb_2NaLaCl_6$, $Rb_2NaGdCl_6$, and Rb_2NaYCl_6)
- Luminescence is observed for all three, which agrees with machine learning predictions
- Single crystals of $Rb_2NaGdCl_6$ and Rb_2NaYCl_6 were successfully grown
- Both have potential to be promising new scintillator materials
- Future work will involve
  - Analyzing compositional uniformity
  - Optimizing growth for larger size crystals
  - Exploring additional compositions from machine learning predictions